Intermediates in the Decomposition of Aliphatic Diazo-compounds. Part 15.[1] Radical Cations in the Decomposition of Diazodiphenylmethane by Copper(II) Perchlorate and by Tris(*p*-bromophenyl)ammoniumyl Perchlorate

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The kinetics and products of the decomposition of diazodiphenylmethane by copper(II) perchlorate and by tris-(*p*-bromophenyl)ammoniumyl perchlorate in acetonitrile solvent have been investigated. The similarity of the two reactions suggests that both the copper and the ammoniumyl salt act as initiators of a chain decomposition in which the chain carriers are radical cations. E.s.r. studies of reaction mixtures in other solvents, notably n-heptyl cyanide, indicate that two different radical cations are formed during the reaction; one, detectable at low temperatures, is believed to be the radical cation formed by simple removal of one electron from the diazoalkane by the initiator, and the other is shown to be the radical cation of benzophenone azine, one of the products of the reaction. In acetonitrile as solvent the major reaction product is tetraphenylethylene, but the ratio of this olefin to benzophenone azine changes from solvent to solvent and in some cases depends upon whether or not oxygen is present. The addition of water to acetonitrile leads to changes in the rate of decomposition of the diazo-compound with both initiators which indicate progressive, and at water concentrations greater than about 0.3M almost total, incursion of a perchloric acid-catalysed decomposition pathway involving rate-limiting formation of diphenylmethyl cations. This has been confirmed by measurement of the kinetic deuterium isotope effect of replacing the added water by deuterium oxide.

INTEREST continues in the mechanisms by which copper and copper-containing compounds bring about decomposition of diazoalkanes and promote methylene transfer to olefins generating cyclopropanes.[2-4] Special concern has been centred on the nature of the reactive species generated in these processes since they show some of the properties of carbenes, although their behaviour is quantitatively different from that of the free divalent carbon compound.[5] The term 'copper-carbenoid' is usually employed,[6] and there has been much discussion of the oxidation state of copper in such intermediates.

Previously [3] we showed that diazodiphenylmethane is decomposed catalytically in the presence of copper(II) bromide in homogeneous solution in acetonitrile giving benzophenone and benzophenone azine. The kinetic and product studies showed a complicated pattern which was interpreted quantitatively in terms of rapid initial generation of a copper–carbene complex which could undergo reversible displacement of a bromide ligand by the diazoalkane giving a second copper–carbene complex, the two complexes then being partitioned between azine and ketone formation. However, the oxidation state of copper in the intermediate complexes could not be decided unequivocally, although the balance of evidence seemed slightly in favour of copper(II).

We now report in detail [7] the results of our investigation of the kinetics and mechanism of the decomposition of diazodiphenylmethane in acetonitrile solution brought about by copper(II) perchlorate. The absence of a nucleophilic anion means that the ligands surrounding copper are acetonitrile molecules and it was felt that this might lead to a simplification in behaviour compared with the reaction catalysed by copper(II) bromide. Literature values of the oxidation potential of diazodiphenylmethane [8] and copper(I) [9] are almost identical in acetonitrile solution, and it was suspected that an electron-transfer mechanism might be important when copper(II) perchlorate was the catalyst. Kinetic and product studies were therefore supplemented by electron spin resonance (e.s.r.) spectroscopic investigation of related reaction systems. As part of the mechanistic proof it was shown that decomposition of the diazoalkane could be initiated using the stable radical-cation salt tris(*p*-bromophenyl)ammoniumyl perchlorate, and kinetic and product studies are also reported for this reaction.

RESULTS

We have confirmed that in acetonitrile solutions of copper(II) perchlorate, electrochemical reduction occurs at +1.0 V (*vs.* SCE). It has been reported that at a rotating platinum disc electrode the oxidation potential of diazodiphenylmethane is 0.95 V. A simple redox reaction between copper(II) perchlorate and the diazoalkane is, therefore, possible in acetonitrile. We have further confirmed by cyclic voltammetry in acetonitrile/0.1M sodium perchlorate that the radical-cation salt tris(*p*-bromophenyl)-ammoniumyl perchlorate undergoes reversible reduction at 1.04 V.[10] Benzophenone azine is oxidised to the radical cation under these conditions at 1.68 V.

Treatment of an acetonitrile solution of diazodiphenylmethane with a catalytic amount of copper(II) perchlorate gives rise to a transient deep blue colour ($\lambda_{max.}$ *ca.* 650 nm) which disappears within a few seconds. The intensity of this colour increases with increasing copper perchlorate concentration, and at temperatures of less than *ca.* −40 °C the colour is stable over a period of hours. At the diazoalkane concentrations ($\sim10^{-2}$M) and copper(II) perchlorate concentrations (10^{-4}—10^{-3}M) normally used in our kinetic and product studies, the blue colour is not detectable; a smooth decrease in the absorbance due to the diazoalkane (526 nm) was observed and this permitted study of the kinetics of the reaction. When the decomposition is complete the reaction solution appears colourless, in contrast to the slowly developing green colour in spent reaction mixtures in which copper(II) bromide was the catalyst,[3] but reaction starts again on addition of further diazoalkane. The principal reaction product is tetraphenylethylene.

Tetraphenylethylene is the major product of oxidation of diazodiphenylmethane at a platinum electrode and chromoamperometric measurements indicate that the electrochemical oxidation is a chain process;[8] the copper(II) perchlorate reaction would thus appear to be of a similar nature. However, in order to establish whether any additional function can be ascribed to copper(II) over and above its role as a one-electron oxidising agent, diazodiphenylmethane was also treated with a quite different, organic, one-electron oxidant, tris(*p*-bromophenyl)ammoniumyl perchlorate. On mixing acetonitrile solutions of the diazoalkane and the ammoniumyl salt the blue colour of the amine radical cation is instantaneously discharged and the red colour of the diazoalkane then disappears at a conveniently measurable rate. Again the major reaction product is tetraphenylethylene.

The disappearance of diazodiphenylmethane in the presence of catalytic concentrations of copper(II) perchlorate or of tris(*p*-bromophenyl)ammoniumyl perchlorate obeys a simple first-order kinetic law. Rate coefficients ($k_{obs.}$) for various concentrations of the catalysts are compared in Table 1, and both sets of results show a linear dependence of $k_{obs.}$ on the oxidant concentration. For copper(II) perchlorate, $k_{obs.}/s^{-1} = 112[Cu(ClO_4)_2] - 0.009\,1$, and for the ammonium salt, the expression is $k_{obs.}/s^{-1} = 117[Ar_3NClO_4] - 0.009\,3$. Within the limits of experimental error, which are probably determined by the purity of the ammoniumyl salt, these relationships are indistinguishable, the expression for the combined results being $k_{obs.}/s^{-1} = 115[\text{Oxidant}] - 0.009\,25$. The negative intercept indicates that no decomposition of diazodiphenylmethane occurs at oxidant concentrations less than *ca.* 8×10^{-5}M. The presence of a readily oxidisable impurity in the reaction system could be responsible for this. Assuming a 1 : 1 stoicheiometry in the reaction of this impurity with the oxidant, its concentration amounts to about 0.5% of the concentration of the diazoalkane.

TABLE 1

Observed first-order rate coefficients ($k_{obs.}$) for the decomposition of diazodiphenylmethane (1.66×10^{-2}M) in acetonitrile at 30 °C induced by copper(II) perchlorate and by tris(*p*-bromophenyl)ammoniumyl perchlorate

10^4[Oxidant]/M	$10^2k_{obs.}/s^{-1}$	
	$Cu(ClO_4)_2$	$Ar_3N^{\cdot+}ClO_4^-$
1.11		0.32
1.33	0.59	0.64
1.55	0.77	
1.66		1.06
2.00	1.42	
2.11		1.56
2.44	1.87	
2.66	2.00	2.16
2.88	2.34	
3.22		2.84

The kinetic evidence points clearly to a mechanism of decomposition of the diazoalkane which is initiated by rapid one-electron oxidation, whereafter the nature of the oxidant used is of no consequence. It was confirmed that the reduced form of the two initiators, copper(I) perchlorate and tribromotriphenylamine, have no appreciable kinetic effect at the concentrations at which they are produced in these reactions. Copper(I) perchlorate is, however, capable of bringing about decomposition of diazodiphenylmethane but the second-order rate coefficient ($k_{obs.}$/[catalyst]) is some 300 times smaller than for the reaction with copper(II) perchlorate.[11] A series of experiments was conducted with both copper(I) and copper(II) perchlorate present, the formal ratio Cu^I/Cu^{II} being in the range 0.67—2.67 with the initial copper(II) perchlorate concentration fixed. The disappearance of the diazoalkane slows down progressively as the concentration of added copper(I) increases (Figure 1) and, at the highest copper(I) concentrations, the reaction follows a kinetic law which is second order in diazodiphenylmethane.

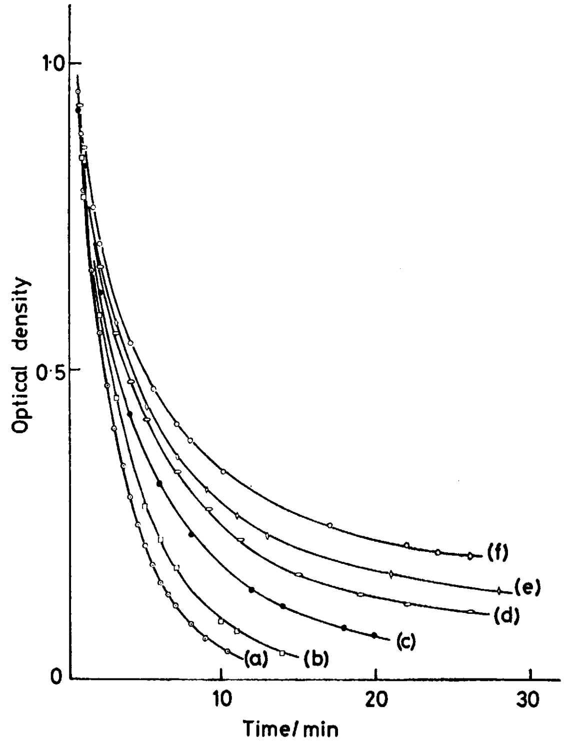


FIGURE 1 Influence of copper(I) perchlorate on the rate of decomposition of diazodiphenylmethane induced by copper(II) perchlorate (1.33×10^{-4}M) in acetonitrile at 30 °C. Concentrations of added copper(I) perchlorate and kinetic order in diazoalkane: (a) None, 1; (b) 9×10^{-5}M, 1—2; (c) 2.2×10^{-4}M, 1—2; (d) 2.7×10^{-4}M, 2; (e) 3.1×10^{-4}M, 2; (f) 3.5×10^{-4}M, 2

Further confirmation that the copper(II) and tris(*p*-bromophenyl)ammoniumyl perchlorates are initiators of the same reaction comes from the product proportions in Table 2. The two salts give rise to the same products in very similar amounts. Above initiator concentrations of 8×10^{-5}M, the principal product is tetraphenylethylene formed in a proportion which changes little with the initiator concentration. Small amounts of benzophenone azine, benzophenone, diphenylmethanol, and benzpinacol are also found. Below initiator concentrations of 8×10^{-5}M the reaction becomes very much slower than at the higher concentrations, and results in the formation of much larger amounts of benzophenone azine at the expense of tetraphenylethylene, and of material (presumed polymeric) which was not detectable by our g.l.c. analytical technique. Such products have been observed previously in the thermal decomposition of diazodiphenylmethane in anhydrous acetonitrile.[12]

The presence of diphenylmethanol, benzophenone, and benzpinacol among the reaction products suggested to us that traces of residual water in the solvent were participating in the product-determining steps of the reaction. Since such participation would lead to the generation of protons in the reaction medium, the possibility exists that the reaction observed in these systems is largely the perchloric acid-catalysed decomposition of diazodiphenylmethane, a reaction known to give mainly tetraphenylethylene.[13] The effect of addition of water and deuterium oxide on the reactions initiated by copper(II) and tris(*p*-bromophenyl)-ammoniumyl perchlorates was therefore investigated; kinetics results are in Table 3.

Although some divergence in rate coefficient was observed between the two catalysts, both show the same general pattern of behaviour. Progressive increase in the concentration of added water causes the observed rate coefficient to rise initially, pass through a maximum (at *ca.* 0.25M-H_2O and *ca.* 0.1M-D_2O), and then fall, the kinetic isotope effect rising steadily throughout. The rate decrease at the higher concentration of added water is characteristic of the perchloric acid-catalysed reaction, and a kinetic isotope effect ($k_{obs.}^{H_2O}/k_{obs.}^{D_2O}$) of 3.25 at 0.66M water has been reported previously.[13] We have confirmed in the present investigation that, at water concentrations greater than 0.25M, perchloric acid and copper(II) perchlorate induce the decomposition of diazodiphenylmethane at rates which are identical within experimental error (see Table 4). At low concentrations of added water and in anhydrous acetonitrile, the rate of decomposition of the diazoalkane induced by one-electron oxidants falls far below the rate with perchloric acid, and the absence of a kinetic isotope effect confirms that proton transfer is not a significant mechanism in acetonitrile without added water. The products of reactions in aqueous acetonitrile (Table 5) further attest to the similarity of the reactions initiated by copper(II) and tris(*p*-bromophenyl)ammoniumyl perchlorates. A noteworthy feature of the product proportions is the increase in the percentage transformation of the diazo-compound into benzophenone azine as the water content of the reaction medium increases: this contrasts with the steady reduction in the yield of tetraphenylethylene.

TABLE 2

Product distribution from the decomposition of diazodiphenylmethane (1.66 × 10^{-2}M) in anhydrous acetonitrile at 30 °C

$10^4[Cu(ClO_4)_2]$/M	Products (%) [a]				
	$Ph_2C{:}CHPh_2$	$Ph_2C{:}N{\cdot}N{:}CHPh_2$	Ph_2CHOH	Ph_2CO	$(Ph_2COH)_2$
2.88	88.5	Trace	Trace	Trace	Trace
2.44	85.8	Trace	2.8	Trace	Trace
1.55	85.3	1.5	2.2	1.8	
1.33	84.3 (79.6) [b]	2.3 (3.8) [b]	3.5 (5.8) [b]	2.2 (2.5) [b]	1.8 (2.0) [b]
1.10	76.8	5.8	4.8	3.2	
0.80 [c]	45.7	16.7	6.6	7.8	
0.55 [c]	24.3	28.3	7.8	10.9	
0.38 [c]	10.8	33.8	6.2	12.3	
0.30 [c]	9.5	32.5	6.0	13.0	

[a] Percentage of initial diazoalkane converted into each product. Where no figure is given, that product was not determined. [b] Figures in parentheses refer to a reaction in which tris(*p*-bromophenyl)ammoniumyl perchlorate was the catalyst. [c] Very slow reactions taking from 12 to 72 h for completion.

TABLE 3

Effect of added H_2O and D_2O on kinetics of decomposition of diazodiphenylmethane (1.66 × 10^{-2}M) using copper(II) and tris(*p*-bromophenyl)ammoniumyl perchlorate (1.33 × 10^{-4}M) in acetonitrile at 30 °C

	$Cu(ClO_4)_2$			Ar_3NClO_4		
$[H_2O]_{added}$/M	k_{obs}^{H}/s^{-1}	k_{obs}^{D}/s^{-1}	Ratio	k_{obs}^{H}/s^{-1}	k_{obs}^{D}/s^{-1}	Ratio
0.00	0.59	0.59 [a]	1.0	0.64	0.64 [a]	1.00
0.046	1.64	1.08	1.5	1.07	0.98	1.1
0.11	2.23	1.24	1.8	1.73	1.03	1.7
0.15	2.86	1.17	2.4	1.81		
0.23	3.02	1.10	2.7	2.02	0.89	2.3
0.28	3.09			1.92		
0.35	2.91					
0.46	2.60	0.78	3.3	1.68	0.53	3.2
0.77				0.90	0.31	2.9
0.93	1.44	0.31	4.6		0.24	
1.39	0.81	0.18	4.5			

[a] Experiment using acetonitrile which had been treated with D_2O and then dried in the usual way.

TABLE 4

Effect of added water on the rate of decomposition of diazophenylmethane (1.66 × 10^{-2}M) catalysed by perchloric acid (1.36 × 10^{-4}M)

	$10^2k_{obs.}/s^{-1}$	
$[H_2O]_{added}$/M	$HClO_4$	$Cu(ClO_4)_2$ [a]
0.10	Very fast	2.1
0.20	5.2	3.0
0.35	3.1	2.9
0.50	2.4	2.5
0.70	1.8	1.9

[a] Interpolated.

For the e.s.r. spectroscopic studies acetonitrile was replaced by solvents of lower dielectric constant. Heptyl cyanide proved particularly useful since the diazoalkane decomposition in this solvent shows qualitatively all the features (*e.g.* colour changes) seen in the acetonitrile reaction. Other solvents used were methylene chloride and tetrahydrofuran to which small volumes of acetonitrile or heptyl cyanide were added to assist solution of copper(II) perchlorate; in these solvent mixtures addition of the diazoalkane to the copper salt does not give rise to the transient blue colouration. The change from acetonitrile to less polar solvents brought about changes in the product proportions as shown in Table 6. In heptyl cyanide, unlike acetonitrile, the product proportions seemed to be sensitive to the presence of oxygen.

TABLE 5

Products of the decomposition of diazodiphenylmethane (1.66×10^{-2}M) induced by copper(II) or tris(*p*-bromophenyl)-ammoniumyl [a] perchlorates (1.33×10^{-4}M) in aqueous acetonitrile at 30 °C

$[H_2O]_{added}$/M	Products (%)				
	$Ph_2C{:}CPh_2$	$Ph_2C{:}N{\cdot}N{:}CPh_2$	Ph_2CHOH	Ph_2CO	$(Ph_2COH)_2$
0	84.3 (79.6) [a]	2.3 (3.8)	3.5 (5.8)	2.2 (2.5)	1.8 (2.0)
0.04	75.2 (72.1)	2.8 (3.0)	8.5 (6.7)	2.7 (2.8)	2.8 (2.1)
0.10	72.1 (70.0)	2.0 (2.8)	14.6 (13.0)	4.3 (3.8)	5.6 (4.8)
0.23	58.5 (60.2)	1.1 (1.8)	18.9 (11.5)	7.2 (6.9)	4.6 (5.5)
0.27	51.6 (52.1)	2.5 (2.8)	28.7 (22.0)	4.1 (4.5)	3.8 (4.0)
0.40	30.0 (33.3)	7.8 (6.4)	41.5 (33.0)	10.0 (6.9)	5.0 (4.0)
0.46	26.8 (30.0)	7.0 (8.8)	44.1 (38.5)	5.5 (7.1)	6.5 (4.8)
0.61	14.8 (18.5)	10.0 (8.0)	43.5 (40.0)	6.6 (7.1)	7.0 (5.5)
0.92	15.0 (20.5)	11.8 (8.5)	48.9 (50.0)	8.8 (6.0)	6.0 (5.4)

[a] Figures in parentheses refer to the reaction induced by the ammoniumyl salt.

TABLE 6

The effect of solvent on product proportions in the decomposition of diazodiphenylmethane in the presence of copper(II) perchlorate

		Products (%) [a]			
$10^2[Ph_2CN_2]$/M	$10^4[Cu(ClO_4)_2]$/M	$Ph_2C{:}CPh_2$	$Ph_2C{:}N{\cdot}N{:}CPh_2$	Ph_2CHOH	Ph_2CO
(a) Heptyl cyanide					
23.5	7.14	46.9	38.2	5.6	3.1
	0.80	42.1	49.3	5.2	2.8
21.4	7.14	49.3 (35.5)	25.7 (50.8)	9.5 (6.8)	2.8 (3.1)
14.7	3.94	62.3 (43.0)	9.3 (32.4)	8.1 (10.1)	1.8 (2.7)
7.1	7.14	68.7	2.35	18.2	1.9
3.5	7.14	72.1	2.1	16.1	2.3
(b) Methylene chloride					
18.7	6.5	27.8	55.7	6.1	2.0
12.5	6.5	23.6	52.6	8.2	1.9
6.2	6.5	50.8	28.2	9.2	2.8
1.5	6.5	55.9	12.8	16.1	3.8
(c) Tetrahydrofuran					
16.6	6.9	3.5	74.0	10.8	5.1
12.5	6.9	6.0	75.0	7.5	4.2
8.1	6.9	5.5	76.0	7.0	2.1
4.1	6.9	15.0	72.5	4.5	1.8
2.1	6.9	18.2	61.3	8.2	2.8

[a] Figures in parentheses refer to reactions carried out with rigorous exclusion of oxygen.

By mixing at −60 °C equimolar solutions of diazodiphenylmethane and copper(II) perchlorate in heptyl cyanide, the blue colouration, usually observed only transiently, is quite stable. Such solutions show only very weak and unresolved e.s.r. signals. It is inferred that the species responsible for the blue colour is not a radical. Similar blue colours have been observed on mixing diazodiphenylmethane and copper(II) bromide [3] or, interestingly, tetracyanoethylene.[14]

When catalytic concentrations of copper(II) perchlorate are used {typical initial concentrations: $[Ph_2CN_2] = 2$M; $[Cu(ClO_4)_2] = 10^{-2}$M} in degassed heptyl cyanide in the temperature range 20—40 °C, strong e.s.r. signals develop, becoming particularly intense towards the end of the diazoalkane decomposition. The spectrum [Figure 2(a)] consists of a single envelope of lines of which 31 can be readily resolved. The appearance of the spectrum is very similar to that reported by Gaspar and his co-workers [15] for the radical cation of benzophenone azine generated electrochemically from the parent compound. Confirmation that the spectrum observed in the copper(II) perchlorate reaction is indeed that of benzophenone azine radical cation was provided by our observations of an identical pattern of signals when the azine is treated with antimony pentachloride in methylene chloride solution. Such solutions of the radical cation are light green in colour, but this colour is lost when the solutions are exposed to air. The simulation shown in Figure 2(b) was achieved using the following parameters: a_N, 0.256 (two nitrogens); a_H, 0.128 (four *p*-hydrogens); a_H, 0.063 mT (eight *o*-hydrogens); line width 0.050 mT.

Treatment of diazodiphenylmethane with catalytic concentrations of copper(II) perchlorate in heptyl cyanide at low temperatures (−60 °C initially) leads to a quite different pattern of signals [Figure 3(a)]. The spectrum consists of five groups each comprising seven lines. On raising the temperature slowly, the spectrum is apparently unchanged up to *ca.* 0 °C whereafter it is transformed into the 31-line spectrum (Figure 2) of the radical cation of benzophenone azine. Subsequent cooling of the solution did not reverse the transformation. Under similar conditions in methylene chloride or tetrahydrofuran solution we were unable to detect the 5 × 7-line spectrum: only the spectrum of benzophenone azine radical cation was observed.

The low frequency component of the experimental spectrum [Figure 3(a)] is not likely to arise from the broadness of the lines since some small splittings can be discerned. The most likely sources of this effect are either (i) the presence of a fast equilibrium in the first step shown in our Scheme, or (ii) the superimposition of the spectrum of the diazoalkane radical cation on the unresolved spectrum of the azine radical cation, the latter spectrum becoming dominant (Figure 2) as the temperature of the reaction mixture is raised.

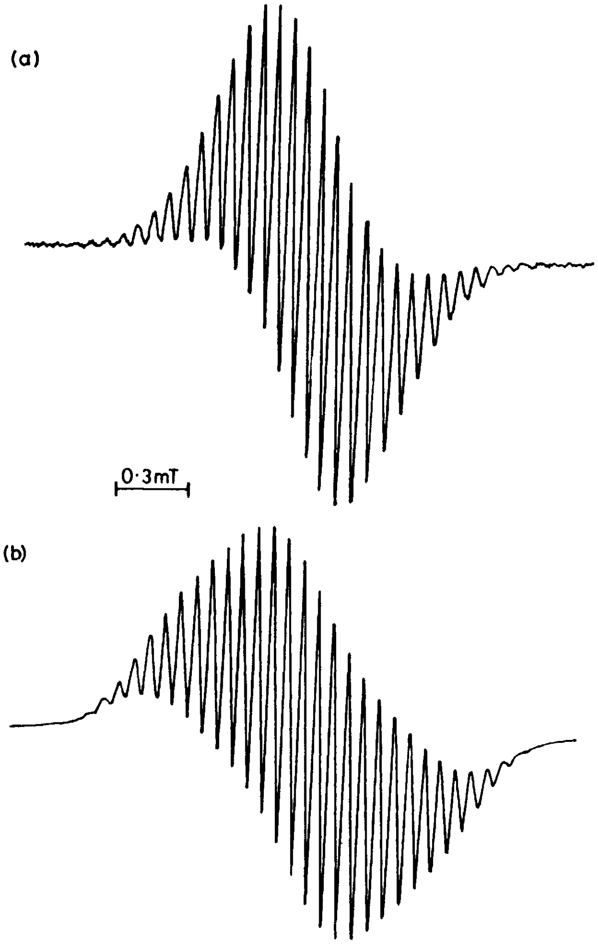


FIGURE 2 (a) E.s.r. spectrum of diazodiphenylmethane (*ca.* 2M) and copper(II) perchlorate (10^{-2}M) in degassed heptyl cyanide at 20 °C. The spectrum was recorded after the reaction was complete. (b) A computer simulation of the spectrum of benzophenone azine radical cation using the hyperfine splitting constants given in the Discussion

9-Diazofluorene on treatment with copper(II) perchlorate in heptyl cyanide or antimony pentachloride in methylene chloride at temperatures below 20 °C gives an e.s.r. spectrum (Figure 4) consisting of five rather broad lines. These could not be further resolved.

DISCUSSION

The Mechanism of the Reaction.—The close similarity of both the rates of reaction and the product distribution in anhydrous acetonitrile indicates that copper(II) perchlorate and tris(*p*-bromophenyl)ammoniumyl perchlorate are involved in the decomposition of diazodiphenylmethane only at the very beginning when they initiate the same reaction by rapid electron abstraction from the diazoalkane. Thereafter a chain reaction takes place involving cation-radical intermediates and apparently without termination processes. The problem is to identify the chain carrier.

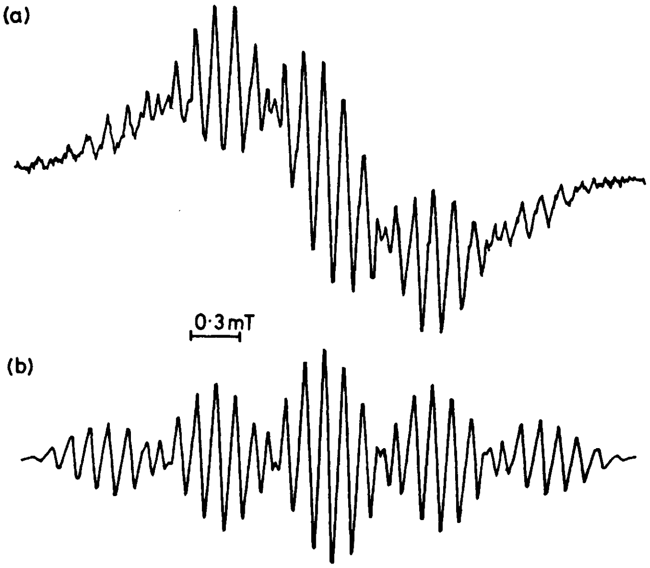


FIGURE 3 (a) E.s.r. spectrum of a degassed solution containing diazodiphenylmethane (*ca.* 2M) and copper(II) perchlorate (10^{-2}M) in heptyl cyanide. The spectrum was recorded at −7 °C before all the diazoalkane had decomposed. (b) A computer simulation of the spectrum of diazodiphenylmethane radical cation using the hyperfine splitting constants given in the Discussion

The kinetic form of the decomposition excludes the possibility that the initially formed diazoalkane radical cation, $Ph_2CN_2^{\cdot+}$, undergoes unimolecular loss of nitrogen to generate the corresponding carbene radical, $Ph_2C^{\cdot+}$. Formation of such a high energy intermediate would be expected to be rate-limiting and, in consequence, the rate law would be expected to show a zeroth-order dependence on the concentration of the diazo-compound.[16] The observed first-order law suggests that the rate-

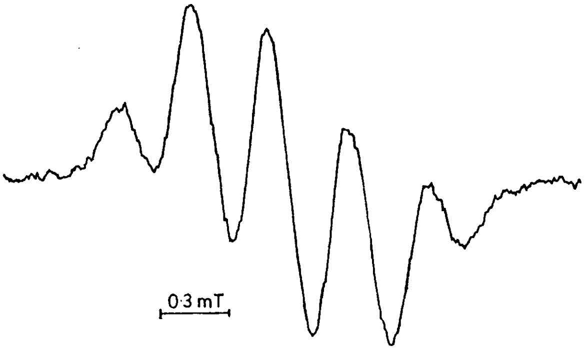
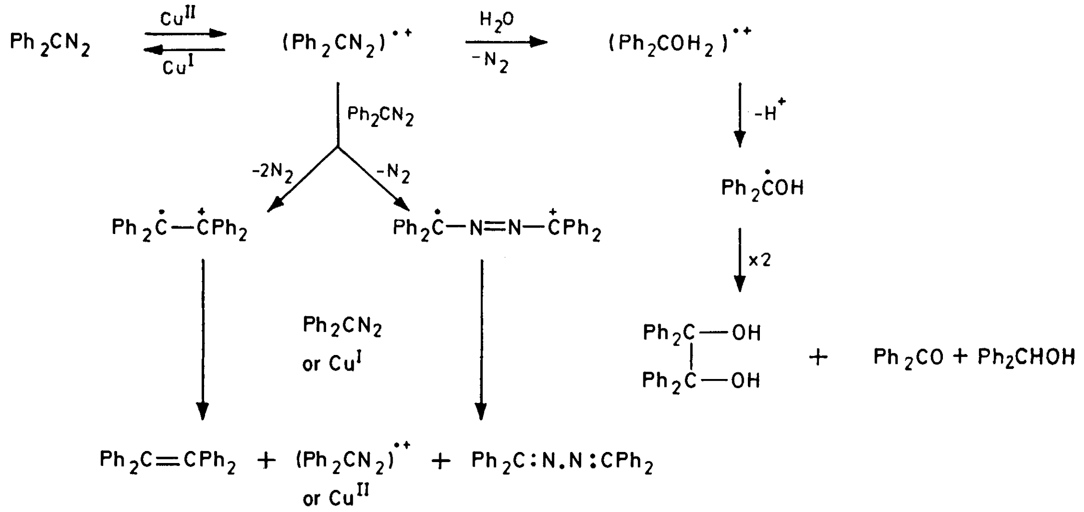


FIGURE 4 E.s.r. spectrum of a degassed solution containing 9-diazofluorene (*ca.* 2M) and copper(II) perchlorate in heptyl cyanide at 20 °C



SCHEME

controlling process is the reaction of $Ph_2CN_2^{\cdot+}$ with a diazodiphenylmethane molecule (rate constant k), and this could occur either at the diazo-carbon atom or at the terminal nitrogen atom of either reactant. Concurrent or subsequent loss of nitrogen would then lead to the radical cations of tetraphenylethylene and benzophenone azine. These radical cations have reduction potentials (*vs.* SCE) of 1.32 [8b] and 1.68 V respectively making them capable of extracting an electron from a further molecule of diazodiphenylmethane ($E_{1/2} = 0.95$ V) or from copper(I) ($E_{1/2} = 1.0$ V) and so completing the reaction chain. Moreover, if the rate-limiting step is indeed the generation of the radical cation of the dimeric olefin or azine, it is not unreasonable that in acetonitrile the preferred reaction mode should be formation of the more stable tetraphenylethylene radical cation. Variation in the ratio of product olefin and azine with change of solvent is also understandable on this basis. We can offer no convincing explanation of the observed effect of oxygen on the product proportions at this time.

The initially generated blue colour does not appear to be associated with significant nitrogen evolution or radical formation. It appears to signify only complex formation, presumably of the charge-transfer type. This may represent a pre-equilibrium in the electron-transfer process which initiates the main decomposition of the diazoalkane. The rate-retarding effect of adding copper(I) perchlorate to the reaction mixture suggests that this initial electron transfer may be reversible (equilibrium constant K). Thus, when three times as much copper(I) perchlorate as copper(II) perchlorate is added to the reaction mixture, the decreasing concentration of diazodiphenylmethane during the course of the reaction alters also the equilibrium concentration of the diazoalkane radical cation; a trend towards a second-order dependence of the rate on the diazoalkane concentration is thus to be expected:

$$\text{Rate} = \frac{kK[Ph_2CN_2]^2[Cu^{II}]}{[Cu^{I}] + K[Ph_2CN_2]}$$

The variation in the rate of disappearance of diazodiphenylmethane with increasing concentration of added water in the reaction medium and the associated increase in production of diphenylmethanol is consistent with the progressive incursion of the perchloric acid-catalysed reaction pathway for which proton transfer is the rate-limiting step. At very low water concentrations (<0.2M) the radical-cation chain mechanism competes with the very rapid acid-catalysed reaction, but at higher water concentrations the consumption of the diazoalkane appears to be almost wholly acid-catalysed as indicated by the kinetic data of Table 4. At the lowest water concentrations and even in nominally anhydrous acetonitrile, some Brønsted acid is expected to be generated by attack of water on the diazoalkane radical cation, giving $(Ph_2COH_2)^{\cdot+}$. The radical $Ph_2\dot{C}OH$ resulting from proton transfer from this radical cation is expected to dimerise or disproportionate. Thus the minor products found in reactions in nominally anhydrous conditions, *viz.*, diphenylmethanol, benzophenone, and benzpinacol can be readily rationalised.

The main features of the proposed reaction pathways are indicated in the Scheme.

E.s.r. Investigation of Radical Cations.—The e.s.r. spectra observed on treatment of diazodiphenylmethane with copper(II) perchlorate at *ca.* 20 °C in heptyl cyanide and its mixtures with methylene chloride may be assigned unequivocally to benzophenone azine radical cation. In deoxygenated solutions the intensity of the spectrum is relatively low while most of the reaction is taking place; it then increases sharply towards the end of the reaction remaining steady thereafter. The final intensity is greater in reaction mixtures containing the higher proportions of methylene chloride in admixture with heptyl cyanide, in agreement with the higher yields of azine in methylene chloride compared with heptyl cyanide. Surprisingly there was no e.s.r. evidence of tetraphenylethylene radical cation in any reaction mixture, despite the fact that in acetonitrile the olefin has a lower oxidation potential than the azine.

The low-temperature e.s.r. spectrum is clearly to be assigned to a chemically different species and not simply to the freezing out of a particular conformer or to some other physical change of the benzophenone azine radical cation which would be expected to be reversible. The general form of the spectrum implies the presence in the radical of two nitrogen atoms with rather similar hyperfine coupling constants. We tentatively assign the spectrum to the radical cation derived by electron removal from diazodiphenylmethane. The simulation shown in Figure 3(b) was achieved using the following parameters: a_N, 0.323 (two nitrogens); a_H 0.115 (two *p*-hydrogens); a_H, 0.057 (four *o*-hydrogens); $a_H < 0.005$ mT (four *m*-hydrogens); line width 0.020 mT. The identity of the a_N-values for the two nitrogen atoms is somewhat surprising, although it is worth noting that the two central nitrogen atoms in diarylpicrylhydrazyle have very similar hyperfine splitting constants.[17] One possible explanation is that for cation radicals the cyclic (diazirine) nuclear arrangement in which the nitrogen atoms are chemically equivalent is more stable than the linear (diazoalkane) form; the reverse order of stability appears to be true for the parent compound.[18]

The cation radical of 9-diazofluorene also has an e.s.r. spectrum (Figure 4) characterised by equal a_N-values (0.34 mT in this instance). We are attempting to carry out INDO calculations on the cation radicals derived from both the diazo-compounds in order to establish their structures in the neighbourhood of the nitrogen atoms.

EXPERIMENTAL

Materials.—Copper(II) perchlorate: a saturated acetonitrile solution of the hexahydrate (10 ml) was refluxed with benzene (200 ml) in a Dean and Stark apparatus until no further water collected. On cooling of the mixture crystals of the anhydrous salt were deposited. These were rapidly filtered off and dried in a vacuum desiccator. Copper(I) perchlorate [$Cu(ClO_4)_2 \cdot 4CH_3CN$] was prepared by reducing the copper(II) salt with copper powder in acetonitrile as described by Hathaway *et al.*[19] The method of Ledwith and his co-workers [20] was used for the preparation of tris(*p*-bromophenyl)ammoniumyl perchlorate.

The diazo-compounds were prepared and the acetonitrile purified as previously described.[13] Other solvents were purified by standard procedures.

Kinetic Measurements.—Reaction rates were determined spectrophotometrically by following the decrease of the absorbance of diazodiphenylmethane at 526 nm using a Unicam SP 1800 spectrometer.

Products.—Analysis of product mixtures was carried out using a Perkin-Elmer F17 gas chromatograph fitted with dual 2 m × 5 mm columns containing 1% OV1 on GasChrom Q. Samples were injected with the column at 150 °C and the temperature was raised to 270 °C at a rate of 5 °C min^{-1}. The instrument was coupled to a Vidar 6300 integrator and response factors were determined relative to fluorene as standard.

Electrochemical Studies.—These were carried out in acetonitrile solution containing 0.1M-tetra-n-butylammonium or sodium perchlorate supporting electrolyte using a platinum button working electrode, a platinum auxiliary electrode, and a saturated calomel reference electrode. For cyclic voltammetry a Chemical Electronics type TR70/2A potentiostat was used in conjunction with a type RB-2 waveform generator. The scan speed was 75 mV s^{-1} in all cases.

E.s.r. Spectra.—Spectra were determined using a Varian E4 e.s.r. spectrometer, fitted with the variable-temperature controller type E4540. The sample tube was connected to two reagent reservoirs through greaseless taps, permitting reactant solutions to be freed of oxygen by repeated freeze–pump–thaw cycles with intermediate flushing with purified nitrogen. The reactant solutions were cooled in their reservoirs, appropriate volumes rapidly mixed and transferred to the sample tube, and the whole apparatus introduced into the spectrometer. In a blank experiment under the conditions used for recording the organic radical cation spectra, copper(II) ions gave only a broad, weak signal which did not appreciably overlap the spectral region of interest. E.s.r. spectra were simulated using a computer program written by Dr. M. F. Chin of the University of York; the program was modified to run on the University of Liverpool ICL 1906S computer.

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